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Some Chemical and Physical Properties of the Effervescent Magnetic Peroxyborates. The Pseudo-Superoxides

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Contribution from the Departments of Chemistry and Physics, Brown University, Providence, Rhode Island, and the Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee. *Received April 23, 1968*

Abstract: Peroxyborate compounds, when heated carefully, can be modified so as to release appreciable quantities of gaseous oxygen when dissolved in water. In addition, these preparations exhibit unusually high paramagnetic susceptibilities. Because of these properties the preparations have been given the acronym EMPB (from Effervescent Magnetic Peroxy Borates). A monotonic relation was found between the amount of gaseous oxygen released on solution and the concentration of paramagnetic centers. Electron spin resonance measurements have resolved three magnetic centers and two of these have been identified as O_2^- and O_3^-; the third is a peroxyborate radical. A fourth center was resolved and identified in irradiated specimens. All centers are due to various chemically bound forms of oxygen. A quantitative discrepancy between the number of spins contributing to the resonances and the number of spins contributing to the susceptibility suggests the presence of O_2 molecules. Using the ^{18}O isotope, the path of oxygen atoms during preparation and aqueous decomposition was charted; only peroxide oxygen atoms end up in the evolved O_2 gas. The nature of the preparations was investigated using the techniques of X-ray, infrared spectra, reflectance spectra, nmr, and chemical analysis. A number of conclusions concerning structure and mechanism have been reached.

The fact that sodium peroxyborate compounds, when heated carefully, could be modified so as to release significant quantities of gaseous oxygen when mixed with water was discovered by Foerster.[2] Some hydrogen peroxide is simultaneously formed, and this only slowly decomposes. The discovery was extended to a variety of materials by Menzel[3] and others.[4] The effervescent behavior, which does not appear to depend on the nature of the cation but has only been reported for peroxyborates, is reminiscent of the superoxides.[5]

Recently the fact that these unusual compounds are strongly paramagnetic was communicated.[6] We present here additional experimental data on their physical and chemical properties. Similarities to and differences from the normal superoxides are pointed out for these "pseudo-superoxides," for which we will use the symbol EMPB (from Effervescent Magnetic Peroxy Borates).

Experimental Section

$H^{18}O^{18}OH$. Double-labeled peroxide was prepared by the electric discharge method.[7] The $H_2{}^{18}O$ starting material of 97–98% enrichment was supplied by YEDA Research and Development, Ltd. The resulting double-labeled hydrogen peroxide was diluted with 30% H_2O_2 of natural isotopic distribution supplied by FMC Corp.

$NaBO_3 \cdot 4H_2O$. Samples containing a mixture of double-labeled and unlabeled peroxide groups were made from the hydrogen peroxide described above. The peroxide was added to a solution of sodium hydroxide and boric acid. The resulting crystalline precipitate was washed repeatedly with cold water and dried in air. By powder X-ray, the product was shown to be $NaBO_3 \cdot 4H_2O$.

EMPB. Samples used in isotope studies were prepared by thermal treatment in a dry nitrogen atmosphere. The water of hydration in the $NaBO_3 \cdot 4H_2O$ starting material was removed at 60°, and the EMPB samples were formed at 120–130°. Samples used in the esr and magnetic susceptibility studies were supplied by FMC Corp.

Ir Spectra. Spectra were recorded for $NaBO_3 \cdot 4H_2O$, $NaBO_3 \cdot H_2O$, and EMPB samples (in a KBr host matrix) using a Perkin-Elmer 337 spectrophotometer. $NaBO_3 \cdot H_2O$ and EMPB samples were prepared for spectra in a dry nitrogen atmosphere.

Mass Spectra. Spectra were recorded with an Hitachi RMU 6D mass spectrometer.[8] Peak heights for the m/e range 28–36 were recorded. The isotope distribution in the molecular oxygen was determined from the peak heights at m/e values of 32, 34, and 36

Magnetic Susceptibility. The Gouy method was used for the susceptibility measurements. All values of χ_g (gram susceptibility) reported are the average of values obtained at four field strengths. For low-temperature measurements a calibrated copper–constantan thermocouple with four junctions in the low-temperature dewar was used to determine the sample temperature.

Magnetic Resonance Experiments. The electron spin resonance (esr) investigations of the preparations were carried out at microwave frequencies near 9.1 and 35 GHz[9] by means of a Varian Model V-4500 X-band spectrometer and a Varian Model V-4561 Ka-band bridge accessory. The magnetic field was modulated at 100 kHz, and the data were displayed on a recorder as the first derivative of the absorption spectrum. The g values[10] were assigned to spectral

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(8) The mass spectrometer was purchased under a generous NSF equipment grant to Brown University.

(9) The notation "Hz" has the conventional meaning of cycles per second.

(10) Here, the measured g value is defined by $g = h\nu/\beta H$, where h = Planck's constant, ν = spectrometer frequency, β = Bohr magneton, and H = magnetic field position of the feature in question.

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